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LANGBEINITE

BY

BERTRAND L. JOHNSON

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UNITED STATES DEPARTMENT OF THE INTERIOR - BUREAU OF MINES

LANGBEINITE[1]

By Bertrand L. Johnson[2]

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INTRODUCTION

Langbeinite, a comparatively rare mineral that has been reported from only five countries in the entire world, has recently attained considerable economic importance in the United States and Poland. Since September 1940, several hundred thousand tons have been produced in one of the Carlsbad (N. Mex.), potash mines for chemical and fertilizer use. As it is a newcomer in this field, and as it is the source of fertilizers possessing special advantages, notably for soils deficient in magnesium or requiring sulfate fertilizers, a discussion of its properties, occurrences, uses, mining, and treatment is appropriate at this time, when fertilizers are in unusual demand. Langbeinite products are of special interest under war conditions because products similar to those now made from langbeinite were formerly imported from Germany.

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The present known areas in which langbeinite occurs are the Salt Range, Punjab, India; the salt deposits of central Germany; the salt beds of Salzburg and Tyrol in Austria; the potash-bearing deposits of Poland; and the New Mexico-Texas potash basin of the United States.

HISTORY

The mineral which much later was to be identified as a double sulfate of potassium and magnesium and named langbeinite was discovered in 1873 in the Mayo salt mine, at Khewra, Punjab, northwest British India, by Dr. H. Warth, while a collection of Salt Range minerals was being made by the Geological Survey of India for the Vienna Exhibition of 1873. This greenish or reddish white glassy mineral, harder than common salt, occurred in an impure saline bed separating two thick salt beds. In the same year the following analysis of this unknown mineral was made by Tween, of the Geological Survey of India, and published (1)[3] in the catalog to the collection of Indian geological specimens sent to the Vienna Exhibition:

	Percent
Magnesium sulfate.........	58.02
Potassium sulfate	38.00
Potassium chloride.........	3.80
Water	.62
Total................	100.44

In 1887 Mallet (2) recalculated this analysis, omitting the water co and also the potassium chloride, which he considered as doubtless sylvit and obtained magnesium sulfate - 60.43 percent and potassium sulfate - 39.57 percent, figures which he considered did not correspond accurate to any simple ratio between the salts. Neither Tween nor Warth in 187 nor Mallet in 1887 recognized the double-salt nature of the mineral but apparently considered it a homogeneous salt mixture.

The identity of langbeinite was recognized by Zuckschwerdt (3) in Germany from a study of material obtained from borings north of Halbe stadt in 1884 for the Wilhelmshall potash works. He named it langbeini in honor of A. Langbein of Leopoldshall. The discovery was announced i 1891.

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[3] See references at the end of this report.

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In 1899 Mallet (4) stated that reexamination of the mineral from the Mayo mine in India proved that it also was langbeinite.

In 1909 and 1910 Goergey (5) described occurrences of langbeinite in the salt deposits in the Austrian Tyrol and in 1909 one in the Tertiary salt beds of Poland.

W. A. K. Christie, (6) in 1914, describing recent prospecting operations for potash in the mines of the Salt Range in India, announced the further discovery of numerous other occurrences of langbeinite in the Mayo mines worked by the Department of Northern India Salt Revenue, and also an occurrence in a small mine at Nurpur.

In the United States Schaller and Henderson (7), in their report on the mineralogy of the drill cores from the New Mexico and Texas potash field, in 1932 published the first record of the occurrence of langbeinite in that region.

DESCRIPTION

Langbeinite is an anhydrous double sulfate of potassium and magnesium, with the formula $K_2SO_4 \cdot 2\ MgSO_4$, or $K_2Mg_2\ (SO_4)_3$, which gives a theoretical composition of K_2SO_4, 42.1 percent, and $MgSO_4$, 57.9 percent, or K_2O, 22.70 percent, MgO, 19.42 percent, and SO_3, 57.88 percent. Analyses have been made of langbeinite from several of the known localities; these show a range in composition from 20.54 to 22.72 percent K_2O, 18.08 to 19.91 percent MgO, and 56.05 to 57.99 percent SO_3. These analyses follow:

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Analyses of langbeinite

No.	Locality	K_2O, percent	MgO, percent	SO_3, percent	Other constituents, percent
1.	Germany - Wilhelmshall	22.32	19.57	57.69	$MgCl_2$ - 0.22 H_2O - 0.20
2.	Do.	21.08	19.74	57.85	$CaSO_4$ - 0.57 $MgCl_2$ - 0.55 NaCl - 0.43 H_2O - 0.78
3.	Germany - Westeregeln	22.2	19.5	57.4	H_2O - 1.0
4.	Austria - Hall	22.72	19.91	57.99	....
5.	India - Mayo mine	20.54	19.43	56.05	KCl - 3.90 H_2O - 0.62
6.	Do.	22.23	19.08	57.27	NaCl - 0.41
7.	United States - Eddy County, N. Mex.	22.37	19.15	57.44	Na_2O - 0.48
8.	Theoretical	22.70	19.42	57.88	....

1. Average of several analyses (Zuchschwerdt, Ztschr. angew. Chem., 18 p. 350).
2. Average of several analyses (Zuchschwerdt, work cited).
3. Analyst, Wagner (Precht, Ztschr. angew. Chem., 1897, p. 68).
4. Goergey, Tschermak's Min. Pet. Mitteil., N. F., vol. 28, 1909, p. 337.
5. Analyst, Tween (Wynne, Mem. Geol. Survey India, vol. 14, 1878, p. 80)
6. Mallet (Mineralog. Mag., vol. 12, 1900, p. 159).
7. Analyst, J. J. Fahey (Schaller and Henderson, Geol. Survey Bull. 833, 1932, p. 43).

Langbeinite very rarely occurs in crystalline form. It is usually found in massive granular aggregates. It crystallizes in the tetartohedra (pentagonal dodecahedral) class of the isometric system in highly modifi transparent colorless crystals. The mineral, according to Hintze, in som deposits shows grayish, yellowish, reddish, violet, or greenish tones. Th langbeinite of New Mexico ranges from white to pink. The specific gravi of specimens from India, Austria, and Germany ranges from 2.81 to 2.8 Determinations on langbeinite from New Mexico gave 2.858. The hardnes of the mineral is between 3 and 4; its fracture is conchoidal or irregular, and it has no cleavage. The luster is greasy to vitreous, and some specimens have a pearly appearance. Langbeinite is tasteless and only very slowly soluble in water. German langbeinites have reported refractive indexes of 1.533 and 1.535. A determination by Schaller (7) on langbeinit from Eddy County, N. Mex., showed a refractive index of 1.532.

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OCCURRENCE

Langbeinite is a saline residue of the evaporation of sea water and is therefore only associated with salt deposits. Conditions that favor the deposition of langbeinite have been rare. Only in the Permian, Triassic, and the Tertiary are such conditions definitely known. Permian deposits occur in Germany and the United States, Triassic in Austria, and Tertiary in Poland. In India the age of the langbeinite-bearing salt deposits of the Salt Range was formerly thought to be Cambrian or pre-Cambrian, but now they are regarded as possibly of Eocene age, as are some of the other salt deposits of that range, thrust-faulted into their present position under beds of doubtful Silurian age.

Some langbeinite deposits appear to be of primary origin, and others, secondary. Hintze (8) states that the secondary langbeinite of some of the German deposits has resulted from reaction between the potassium chloride and magnesium sulfate of the deposits.

Alterations of langbeinite have been reported. Goergey (5) states that langbeinite at Stebnik in the Polish potash field has altered to a schoenite aggregate, and Mansfield and Lang (9) claim that the langbeinite of New Mexico has altered to kainite and kieserite.

The principal minerals that have been reported in association with langbeinite in the various deposits include halite, schoenite, polyhalite, kainite, sylvite, and kieserite.

USES

Langbeinite deposits in Poland and the United States are of recent commercial importance. Formerly langbeinite from Germany was utilized. The deposits in India and the former Austrian Tyrol are not known to have economic importance.

Langbeinite is used as a raw material for the production of sulfate of potash-magnesia and sulfate of potash for fertilizer purposes in both Poland and the United States. At Stebnik, Poland, langbeinite was produced in the nineteen thirties. Both potassium sulfate, K_2SO_4 (96 percent pure) and a mixed potassium-magnesium sulfate were obtained. The latter was introduced on the Polish market about 1933 under the trade name "Kalimag" for use on soils showing magnesium deficiency, particularly those growing leaf tobacco, fruits, and bushy plants. An analysis of "Kalimag" shows the following composition:

	Percent	
Potassium sulfate (K_2SO_4)	34	(18.4 percent K_2O)
Magnesium sulfate ($MgSO_4$)............	53	
Calcium sulfate ($CaSO_4$)................	2.5	
Sodium chloride (NaCl)..................	3.6	
Potassium chloride (KCl)...............		
Moisture	1.8	
Insoluble	6.0	
Total..........................	100.9	

Turrentine (10) states in his "Potash in North America", in 1943, regarding the langbeinite deposits in the main German potash field that "Difficulties encountered in the refining of langbeinite in Europe, where it occurs in considerable abundance in potash deposits, early led the industry away from that raw material to others more amenable to simplified processing." In the United States the langbeinite deposits of New Mexico have been mined and refined since 1940. Sulfate of potash-magnesia (containing 22 percent K_2O and 18.5 percent MgO), sulfate of potash (48 to 50 percent K_2O), and magnesium chloride have been produced and marketed from the langbeinite mined.

Both sulfate of potash and sulfate of potash-magnesia are valuable plant foods in water-soluble form, the latter being especially valuable because of its relatively slow solubility and its magnesium content. Turrentine (10) states that "a fairly similar product analyzing 26 percen K_2O and 9 percent MgO, both as sulfate, was formerly imported from Europe in quantities averaging 14,000 tons a year and was found to be a useful form of readily soluble magnesium sulfate (as well as potassium sulfate) for agricultural use where immediate availability of that plant food was required. With the termination of foreign supplies this new domestic product found an immediate market."

DOMESTIC DEPOSITS

General Setting

The only deposits of langbeinite now known in the United States occ in the potash-bearing New Mexico and Texas portion of the great northe trending shallow geosyncline of nearly flat-lying Permian rocks, which enclosed between the eastern front of the Rocky Mountains on the west a the pre-Cambrian shield in Minnesota, the Ozark Mountains in Missouri and the Llano-Burnet pre-Cambrian area in central Texas, on the east. These Permian sediments consist chiefly of clay or shale, limestone, dc mite, anhydrite, sandstone, and salt. The salt beds do not outcrop, but drill holes and underground workings have shown that they occur in diffe ent formations in the southern part of the geosyncline and along its east limb from Texas to Kansas and possibly farther north.

The potash-bearing beds occur in the Salado formation, of late Permian age, which underlies some thousands of square miles, largely between the Pecos River in southeastern New Mexico and the Red River in northwestern Texas. The formation has a maximum thickness of about 1,400 feet and is composed essentially of halite, with relatively thin beds of anhydrite, reddish sandy shale, polyhalite, and locally other potash-bearing salts.

The beds of potassium salts lie at depths of about 350 feet to over [illegible] feet below the surface. Potassium minerals include sylvite (KCl), polyhalite (K_2SO_4. $MgSO_4$. 2 $CaSO_4$. 2 H_2O), langbeinite (K_2SO_4. 2 $MgSO_4$), leonite (K_2SO_4. $MgSO_4$. 4 H_2O), carnallite (KCl. $MgCl_2$·6 H_2O), with kainite ($MgSO_4$. KCl. 3 H_2O). The most abundant and widespread potassium-bearing mineral in this formation is reported to be polyhalite. Sylvite, next in order of abundance, is now being mined east of Carlsbad, N. Mex., by three companies, one of which, the International Minerals & Chemical Corporation, is also mining a bed of langbeinite about 100 feet above its productive sylvite bed.

In volume, the potash-bearing salts form only a fractional part of the Salado salt series. They are distributed in beds or bands from a fraction of an inch to several feet in thickness through an interval of 1,500 feet or more of salt and associated beds.

Distribution

Langbeinite is reported by Schaller and Henderson (7), in 1932, to have been found in drill cores from 11 wells, some privately owned and some governmental, as follows:

	Location
McNutt No. 1	Eddy County, N. Mex.
Martin Yates No. 1	Do.
Gypsy No. 3	Do.
Gypsy No. 4	Do.
Martin Yates No. 2	Do.
Ballard No. 1	Do.
Blanchard No. 1	Do.
Blanchard No. 2	Do.
Government No. 12	Winkler County, Tex.
Government No. 13	Eddy County, N. Mex.
Government No. 17	Lea County, N. Mex.

As these records cover an area of several townships, the distribution strongly suggests local areas that may be underlain by beds of langbeinite thick and rich enough to mine if sufficient demand for potassium sulfate should arise. DeVaney and Cooke (11) state that drill records show the presence of beds of langbeinite thick enough to lead to the belief that large amounts are available.

The thickness of the beds containing langbeinite ranges from a trac to nearly 14 feet. The thickest bed of possible economic importance in the drill cores (according to Mansfield and Lang (9) in 1935) was a 5-foot bed with a content of 11.25 percent K_2O, found in a private core test. Occasionally beds of nearly pure (up to 90 percent) langbeinite were shown in the cores. The best recorded was an 11-inch bed, at a depth of 2,534 feet, in Government No. 17 test, which yielded 20.63 percent K_2O. The bed now being mined near Carlsbad is stated by Hubbell (12) to be 5 to 7 feet thick. The greatest observed vertical range of langbeinite in th listed wells was about 100 feet in Government No. 13 well.

The depth to the langbeinite beds ranges from 755 feet (the so-call 800-foot level) in the International mine to 1,631 and 2,513 feet in the government wells Nos. 13 and 17, which lie farther east. The deepest langbeinite beds are in the section between 2,532 and 2,539 feet.

The langbeinite is associated with halite, sylvite, kainite, polyhalit and a little kieserite. Some beds, several feet in thickness, consist essentially of langbeinite and halite. Halite occurs associated with the lan beinite in the International mine, and the bed in places contains so much salt that it is discarded as waste.

Character

The langbeinite in the New Mexico field occurs both in massive, granular form and in tetrahedral crystals. Most of the crystals are sm but one crystal 2 centimeters (three-fourths inch) in length has been observed. Color ranges from white to faint pink. Some of the massive co less varieties are said to resemble granular quartz. Most of it, howeve has a distinctive pink color. The hardness is high for a potash mineral and the langbeinite is reported to be the hardest looking of the saline m als of the field.

An analysis of langbeinite from the McNutt well in Eddy County, Mex., is given by Schaller and Henderson (7) as follows:

	Analysis	Ratios	
K_2O	22.37	0.2371	1.02 or 1
Na_2O	.48	.0077	
MgO	19.15	.4749	1.98 or 2
SO_3	57.44	.7180	3.00 or 3
Loss on ignition	.25		
Insoluble in water	.05		
Total	99.74		

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The ratios obtained correspond closely with the well-established formula, $K_2SO_4 \cdot 2\ MgSO_4$.

Although some of the langbeinite is in beds thick enough to mine and market with little or no treatment, most of it is so low grade that concentration processes will have to be used if these beds are mined later.

Mining Methods

The langbeinite bed of the International Minerals & Chemical Corporation is mined by the room-and-pillar system, with undercutting of the faces. The mining area is just outside the 450-foot radius pillar around No. 1 shaft. Drilling is by air jackhammers with detachable bits. Wet drilling is used, as the dust is reported to be somewhat irritating. Electric caterpillar-mounted loaders serve rubber-tired electrically operated shuttle cars operating on trackless trolley, with overhead two-wire system in the main haulage entry and on extension cables in the rooms. The cars shuttle between the loading faces and the transfer raise without turning.

Treatment

The langbeinite as mined is reduced underground to minus 4-mesh by means of a primary single-roll crusher. This is followed at the surface by further crushing and sizing on vibrating screens. The screened product is delivered to storage bins. This is later "washed" to remove the halite, or common salt, associated with it. Langbeinite and halite are separated by utilizing the greater rate of solubility of the halite in water. Crushed material is delivered from the storage bins to a screw conveyor, which agitates it with water in a trough, where most of the halite is dissolved. Final solution of the halite takes place in a rake classifier, which separates the undissolved langbeinite from the halite brine. The rake product is filtered, dried, and temporarily stored as "washed langbeinite." This material, sold as sulfate of potash-magnesia, contains 22 percent K_2O (40 percent K_2SO_4) and 18.5 percent MgO.

From the temporary storage bins the washed langbeinite then passes either to permanent storage piles from which it is taken for shipment as sulfate of potash-magnesia or is withdrawn as needed to be ground for base exchange and the preparation of potassium sulfate and magnesium chloride.

In the base-exchange process the washed langbeinite is ground in brine in a ball mill in circuit with a simplex classifier, the overflow of which goes to the reaction tanks, where it is treated with potassium chloride in solution for the production of potassium sulfate. In this reaction the potassium chloride in solution and the sulfate of potash-magnesia (langbeinite) exchange bases to yield potassium sulfate and magnesium chloride. The sulfate produced is filtered, dried, and stored. The waste liquor passes to an adjacent plant, where the magnesium chloride is recovered and shipped to the electrolytic plant of the International Minerals & Chemical Corporation at Austin, Tex., for the recovery of metallic magnesium.

A detailed description of the mining and treatment of the langbeinit at this mine in 1941 is given by Hubbell (12).

Production

Production of langbeinite at the mine of the International Minerals Chemical Corporation, near Carlsbad, N. Mex., was begun in the fall of 1940, and the first shipment was made in October of that year. Accordi to Hubbell (12), approximately 55,000 tons were hoisted for refinery use from September 1940 to the end of January 1941. Production figures cov ing the operations since that date are not available for publication.

Prices

Prices of sulfate of potash-magnesia and sulfate of potash are give in the producer's price schedule and in trade journals. Sulfate of potash magnesia — minimum 40 percent K_2SO_4, 18.5 percent MgO — is quoted in Oil, Paint and Drug Reporter in January 1944 at $26.00 per ton ex-vesse at Atlantic and Gulf ports within the United States, in bulk per net ton of 2,000 pounds, minimum carlots of 40 tons. Sulfate of potash, 90/95 perc K_2SO_4 (basis 90 percent K_2SO_4) was quoted at $36.25 per net ton. Seaso discounts are allowed on both commodities.

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